reducing the error below 1 mL because structural isomers often differ by 1 mL in molar volume.

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Effect of Aryl Substituents, Solvent, and Steric Effects on the Efficiency of Excited-State Carbonyl Production from 1,2-Dioxetanes

William H. Richardson,* James H. Burns, Mary E. Price, Richard Crawford, Mark Foster, Penny Slusser, and James H. Anderegg

Contribution from the Department of Chemistry, San Diego State University, San Diego, California 92182. *Received January 9, 1978*

Abstract: The efficiency of triplet carbonyl production was measured for a series of eight variously substituted 1,2-dioxetanes by using stimulated emission from 9,10-dibromoanthracene (DBA). Triplet efficiencies for some of the dioxetanes were also determined by isomerization of *trans*-stilbene. In some instances, singlet (S_1) efficiencies were measured by stimulated light emission from 9,10-diphenylanthracene (DPA). In agreement with most previous reports, high triplet/singlet (S_1) efficiencies were observed. The effect of solvent on the triplet efficiency was pursued with bis(*p*-anisyl)-1,2-dioxetane (DAD). Here, a change from benzene to methanol solvent decreased the triplet efficiency by 440-fold. The results of the efficiency study were interpreted in terms of a biradical mechanism. The variations in efficiency with changes in dioxetane structure and solvent are explained in terms of partitioning the singlet biradical (S_R) between singlet carbonyl products and the triplet biradical (T_R). An increase in the rate of production of T_R is expected to increase the triplet efficiency. In general, triplet efficiencies for most dioxetanes are decreased with strongly electron-releasing groups, while triplet efficiencies are increased with increased steric effects. An approximate empirical correlation was noted between the activation energy for thermolysis of dioxetanes and the triplet efficiency (α_{T_1}): % $\alpha_{T_1} = 7.24E_a - 156$, where S_{yx} (the standard error estimate of α_{T_1} on E_a) is ±8.4%. From an analysis of the solvent effect on α_{T_1} for DAD, a minimum value of $\Delta G^{\ddagger} = 4$ kcal/mol could be set for the decomposition of the singlet biradical to ground-state carbonyl products in benzene solvent.

A select few classes of molecules possess the ability to produce electronically excited state products in a chemical reaction.[1] Dioxetanes are one class of molecules that can accomplish this feat in the course of thermal decomposition. Of added interest is the observation that ground-state singlet dioxetanes produce excited-state carbonyls that are largely in the triplet state.[1j] Understandably, the thermolyses of 1,2-dioxetanes have recently been an active area of investigation with the hope of unraveling the mechanism whereby triplet products result from a ground-state reactant.

A large portion of our previous work in this area has dealt with a kinetic analysis of various substituted dioxetanes, with the goal of gaining some insight to the mechanism of the thermolysis.[2] We now report the measurements of efficiencies of excited carbonyl production from the thermolysis of these substituted dioxetanes. Our intention was to see how structural modification of dioxetanes affected the efficiency of excited-state carbonyl formation and if these effects could be rationally correlated with our previous mechanistic studies. We have also used solvent variation as a probe to determine the interrelationship between the mechanism of dioxetane thermolysis and excited-state carbonyl production. Some tentative conclusions have been made, but it is clear that this is just a step in understanding the factors that govern the efficiency of excited-state carbonyl production from dioxetanes.

Results

Preparation of the substituted 1,2-dioxetanes that were used in this study was previously reported.[2] The primary method of determining efficiencies of excited-state carbonyl products, formed from the dioxetanes, was by light emission methods. These methods have been employed in other laboratories and are probably the most convenient method of determining efficiencies.[3,4] In addition, the methods employing 9,10-dibromoanthracene (DBA) and 9,10-diphenylanthracene (DPA) as acceptors provide a unique method of counting triplet and singlet excited-state alkyl carbonyl products.[4]

With DBA as the excited-state energy acceptor in the thermolysis of a dioxetane, the apparent quantum yield (Φ_{App})

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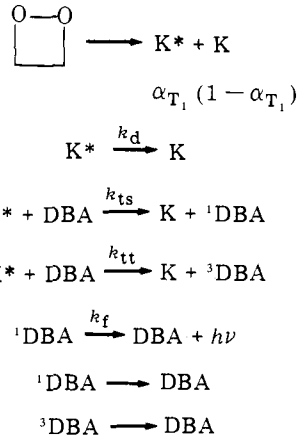
Scheme I



of chemiluminescence (CL) is given by

$$\Phi_{App} = I_n \text{ (einsteins)/mol dioxetane decomposed} \quad (1)$$

$$\Phi_{App} = \alpha_{T_1}\Phi_{ET}\Phi_f^{DBA} \quad (2)$$

Here, I_n is the integrated light intensity, α_{T_1} is the efficiency of triplet carbonyl production, Φ_{ET} is the energy transfer quantum yield to DBA to give singlet DBA, and Φ_f^{DBA} is our measured quantum yield for DBA fluorescence. From Scheme I and eq 2, one obtains eq 3, where K corresponds to the carbonyl products. One can calculate $1/\Phi_{App}$ from eq 1, where the integrated light intensity produced from the thermolysis of the dioxetane in the presence of DBA is measured by a photomultiplier tube. The integrated light intensity (I_n) is calculated from eq 4, where I_{f_0} is the light intensity at time

$$1/\phi_{App} = \frac{1}{\alpha_{T_1}\Phi_f^{DBA}}\left[\frac{k_{ts}+k_{tt}}{k_{ts}} + \left(\frac{k_d}{k_{ts}}\right)\frac{1}{[DBA]}\right] \quad (3)$$

$$I_n = I_{f_0}\left[\frac{1}{k} - \frac{e}{k}^{-kt_\infty}\right] \quad (4)$$

zero, k is the rate coefficient for decay of light intensity, and t_∞ is time infinity. The approximation is made that $t_\infty \simeq 10t_{1/2}$ in order to calculate I_n. The photomultiplier system was calibrated by using the α_{T_1} value for 3,3-dimethyl-1,2-dioxetane (DMD), which was obtained by the *trans*-stilbene isomerization method (vide infra). Considering eq 3, a plot of $1/\Phi_{App}$ vs. $1/[DBA]$ gives an intercept of $1/\alpha_{T_1}\Phi_f^{DBA}[(k_{ts}+k_{tt})/k_{ts}]$. With our measured value of Φ_f^{DBA} and literature values for k_{ts} and k_{tt},[4] one can calculate α_{T_1}. In a similar manner, the efficiency of excited-state singlet carbonyl formation (α_{S_1}) was obtained with DPA as the acceptor. Here, a plot of $1/\Phi_{App}$ vs. $1/[DPA]$ gives an intercept of $1/\alpha_{S_1}\Phi_f^{DPA}$. From this intercept and our measured value of Φ_f^{DPA}, one obtains α_{S_1}.

An alternative method to obtain efficiencies was also used, which depends on the isomerization of *trans*-stilbene by the excited carbonyl products.[5,6] The apparent quantum yield (Φ_{App}) by this method is given by

Φ_{App}
= mmol *cis*-stilbene formed/mmol dioxetane decomposed (5)

$$\Phi_{App} = \alpha_{T_1}\Phi_{ET}\Phi_{t\rightarrow c} \quad (6)$$

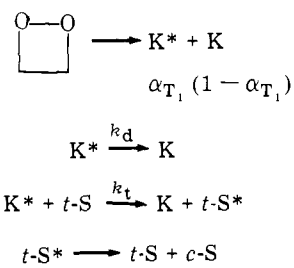
where Φ_{ET} is the energy transfer quantum yield and $\Phi_{t\rightarrow c}$ is the quantum yield for *trans*- to *cis*-stilbene isomerization. From Scheme II, where *t*-S is *trans*-stilbene and *c*-S is *cis*-stilbene, eq 7 results from eq 6. By GLC analysis, the millimoles of *c*-S produced are obtained, and $1/\Phi_{App}$ is calculated from eq 5. A plot of $1/\Phi_{App}$ vs. $1[t\text{-S}]$ gives $1/\alpha_{T_1}\Phi_{t\rightarrow c}$ as the intercept and α_{T_1} is calculated with a literature value for $\Phi_{t\rightarrow c}$ (0.55).[7]

Table I. Triplet (α_{T_1}) and Singlet (α_{S_1}) Efficiencies of Carbonyl Products from Dioxetanes at 45 °C in Benzene

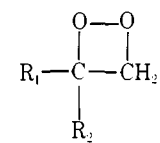
dioxetane	% α_{T_1} (*t*-S)[a]	% α_{T_1}(DBA)[b]	% α_{S_1}(DPA)[c]	α_{T_1} (DBA) /α_{S_1} (DPA)
DMD	13	≡13	5.4×10^{-2}	240
PMD	16	14	9.5×10^{-2}	145
DPD	3.5[5]	1.2		
DBD		22	0.76	29
TPD		1.9		
DAD		0.41		
DAD-(MeOH)[d]		0.93×10^{-3}		
TMD[e]		36	0.43	83

[a] By *trans*-stilbene isomerization. [b] By light emission from DBA. [c] By light emission from DPA. [d] In methanol solution. [e] At 70.1 °C.

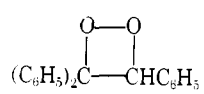
Scheme II



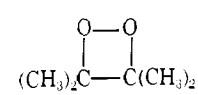
The results of the efficiency measurements by light emission with DBA and DPA and by *trans*-stilbene isomerization are given in Table I. Our values for TMD are in good agreement



DMD, $R_1 = R_2 = CH_3$
PMD, $R_1 = CH_3$; $R_2 = C_6H_5$
DPD, $R_1 = R_2 = C_6H_5$
DBD, $R_1 = R_2 = C_6H_5CH_2$
DAD, $R_1 = R_2 = p\text{-}CH_3OC_6H_4$



TPD



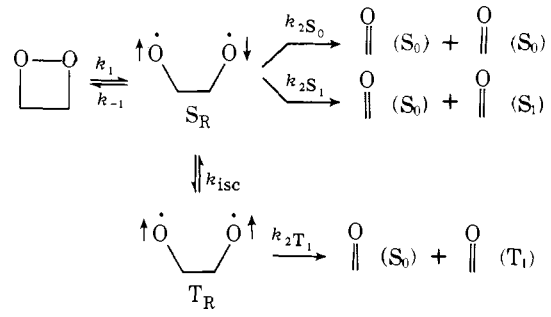
TMD

with those reported by Wilson, Golan, Harris, and Baumstark (α_{T_1} = 30%, α_{S_1} = 0.15%),[8] considering the potential experimental error in the method.

Discussion

Our previous substituent effect studies have led us to conclude that the thermolysis of simply substituted dioxetanes is most conveniently explained in terms of a biradical process (Scheme III).[2] Recently, added support for this mechanism

Scheme III



has been provided by Koo and Schuster[9] in a isotope effect study with *trans*-3,4-diphenyl-1,2-dioxetane. Also, the recent general valence bond calculations of Harding and Goddard[10] are in good agreement with the biradical process. We now proceed to consider substituent and solvent effects upon the efficiency of excited-state carbonyl formation in view of the biradical mechanism. In the evaluation of the efficiency data, small differences are not considered to be significant. Since the efficiencies are obtained by extrapolation to infinite acceptor concentration, inherent error will be encountered here. Also, there is the possibility that impurities could alter efficiencies; however, this source of error should be minimized by the procedure of extrapolation to infinite acceptor concentration.

First, let us consider the effect of aryl substituents on the efficiency of excited-state carbonyl production. It is seen from Table I that the efficiency decreases significantly from DMD when two or three phenyl groups are substituted on the dioxetane ring. In addition, a further decrease in efficiency is noted when aryl groups are substituted with *p*-methoxy groups in proceeding from DPD to DAD. These trends in efficiencies can be interpreted in terms of the biradical mechanism, where the production of S_0 and T_1 carbonyl products from the biradical S_R is competitive. With increased phenyl or *p*-methoxyphenyl substitution, rupture of the C-C bond in S_R becomes more facile relative to intersystem crossing of S_R to T_R. That is, with increased phenyl or *p*-methoxyphenyl substitution, S_R decomposes to carbonyl products at the expense of producing T_R and subsequently triplet carbonyl species. Since the decomposition of S_R produces mainly S_0 carbonyl species, a decrease in the overall efficiency of excited-state carbonyl formation results.

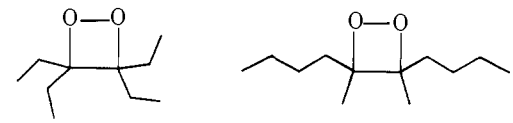
Another significant decrease in efficiency is noted when the solvent is changed from benzene to methanol. With DAD, this solvent change decreases the efficiency by about 400-fold (= $0.41/0.93 \times 10^{-3}$). Again, this decrease in efficiency upon changing from an aprotic to a protic solvent can be conveniently explained in terms of the biradical scheme. Such a change from an aprotic (benzene) to a protic (acetic acid) solvent was found to lower the enthalpy of activation for *β*-scission of the *tert*-butoxy radical to acetone and methyl radical.[11] A similar reduction in the activation energy for decomposition of the singlet biradical (S_R) to carbonyl products is expected upon changing the solvent from benzene to methanol. Since intersystem crossing to S_R to T_R is not expected to be appreciably altered by the solvent change,[12] S_R is diverted preferentially by methanol solvent to singlet carbonyl species. This occurs at the expense of generating triplet carbonyl species via T_R and lowers the overall efficiency.

Given the 440-fold decrease in efficiency upon changing from benzene to methanol solvent with DAD, one can estimate the change in the free energy of activation ($\delta\Delta G^{\ddagger}$) for step k_{2S_0} with this solvent change. With the approximation that k_{isc} is unaltered by the solvent change[12] and with the observation that $k_{2S_0} \gg k_{2S_1}$ based on efficiency measurements, the 440-fold decrease in efficiency can be associated with step k_{2S_0}. With $k_{2S_0}(\text{MeOH})/k_{2S_0}(\text{benzene}) \simeq 440$, $\delta\Delta G^{\ddagger} \simeq 3.9$ kcal/mol at 45 °C, which may be compared to $\delta\Delta H^{\ddagger} = 6$ kcal/mol for the *β*-scission of the *tert*-butoxy radical in changing from benzene to acetic acid solvent.[11] In addition, the value of $\delta\Delta G^{\ddagger} = 3.9$ kcal/mol sets a minimum value for $\Delta G^{\ddagger}$ of the k_{2S_0} process for DAD in benzene solvent.

It also appears that steric effects may play a role in determining the efficiency of excited-state carbonyl production. From Table I it is noted that the efficiency is increased nearly threefold in proceeding from DMD to TMD. Also, the efficiency almost doubled in proceeding from DMD to DBD. With both TMD[8] and DBD,[2d] increased activation energies were observed relative to DMD,[2e] which were interpreted in terms of steric effects associated with the biradicals.[2d,13]

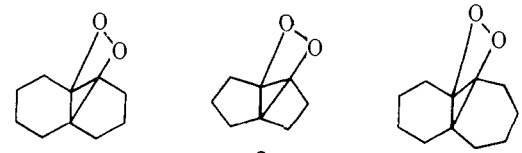
The involvement of steric effects in the efficiency of excited-state carbonyl production from dioxetanes can be further pursued by considering data from other laboratories. The efficiencies of PMD (10%) and 3,4-diphenyl-3,4-dimethyl-1,2-dioxetane (DPMD) (35%) were reported relative to TMD[14] and we have indicated these efficiencies relative to our value for TMD (36%). Again, one observes increased efficiency with an increase in steric effects, which are also reflected in the E_a values for PMD (22.9 kcal/mol)[2e] and its symmetrical analogy DPMD (25 kcal/mol).[14]

The triplet efficiencies of tetraethyl-1,2-dioxetane (TED) and 3,4-dimethyl-3,4-di-*n*-butyl-1,2-dioxetane (DMBD) were reported to be 50 and 25%, respectively.[15,16] Arrhenius activation energies for TED and DMBD are 30.0 and 25.2 kcal/



TED DMBD

mol, respectively.[15] Here too, the increased steric effects, as reflected in the activation energies, correlate with an increase in efficiency. A similar trend between steric effects, as reflected in activation energy, and efficiencies is seen in the tricyclic dioxetanes shown below.[17] For comparison to our results the efficiencies are normalized to our TMD value of 36%, whereas the TMD value reported with the series is 22%.[17] The reported Arrhenius activation parameters are shown with **1–3** in kcal/mol.[17]



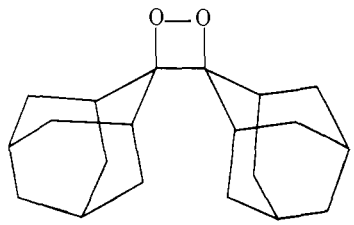
1 **2** **3**

1.3% 13% 21%
23.0 25.6 29.8

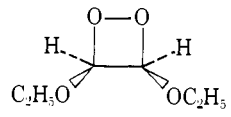
To interpret the variation in α_{T_1} with steric effects, in the context of the biradical mechanism, requires that the rate of decomposition of S_R to carbonyl products decreases relative to intersystem crossing of S_R to T_R with increased steric effects. Since the rates of both of these processes could change with varying steric effects, a detailed interpretation is not warranted at present.

In the above analysis, the variation in efficiency of triplet carbonyl production was rationalized in terms of a partitioning of the singlet biradical (S_R) to singlet carbonyl products vs. intersystem crossing to the triplet biradical (T_R). Electron-releasing substituents facilitate the partitioning of S_R to carbonyl products, while steric effects favor partitioning of S_R to T_R and subsequently to triplet carbonyl products. Increased

steric effects are reflected in higher activation energies of dioxetane thermolysis and in some instances strong electron-releasing substituents may lower the activation energy. Thus, an empirical correlation of activation energy for dioxetane thermolysis vs. triplet carbonyl efficiency (α_{T_1}) may result. A tabulation of activation energies and triplet efficiencies that have been reported is given in Table II. Where it was possible, the efficiencies were normalized to TMD (α_{T_1} = 36%). A least-squares fit gives % $\alpha_{T_1} = 7.24E_a - 156$, where S_{yx} (the standard error estimate of % α_{T_1} on E_a) is ±8.4%, with dioxetanes **3, 5,** and AD excluded from the correlation. Although



AD



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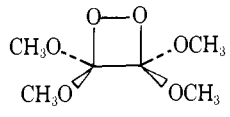

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the correlation is crude, the error in predicting α_{T_1} (±8.4%) approaches the experimental error for many of the dioxetanes. The success of such a correlation depends upon a similar response to electronic and steric effects in the rate-determining step (k_1) vs. the steps leading to singlet and triplet carbonyl formation via S (Scheme III). This criterion may not be met in the cases where significant deviation from the correlation is observed (e.g., with dioxetanes **3, 5,** and AD).

In summary, efficiency variations in producing excited-state carbonyl products from dioxetanes, that are related to structure and solvent changes, can be rationalized in terms of a biradical process (Scheme III). The explanations are based on the partitioning of the singlet biradical (S_R) between singlet carbonyl products and the triplet biradical (T_R). In general, triplet efficiencies for most dioxetanes are decreased with strongly electron-releasing groups, while triplet efficiencies are increased with increased steric effects. Since the steric effects and sometimes the electronic effects of substituents are reflected in the activation energy for thermolysis of dioxetanes, an empirical correlation of E_a vs. α_{T_1} was made. The correlation predicts the triplet efficiency (% α_{T_1}) for most of the dioxetanes to within ±8.4%. Although many of the features of efficiency can be rationalized by the biradical process (Scheme III), a considerable amount of additional data is required to support these proposals.

Experimental Section[21]

Materials. The preparation of the dioxetanes DMD,[2e] PMD,[2e] DPD,[2d] DBD,[2d] TPD,[2b] DAD,[2a] and TMD[19] were reported previously. DBA was purified by recrystallization from xylene. Scintillation grade (MCB) *trans*-stilbene was recrystallized three times from cold absolute ethanol in a darkened room. Spectroquality benzene (MCB) was further purified by washing with concentrated sulfuric acid and water and then drying over calcium chloride. The dried benzene was refluxed over phosphorus pentoxide and then distilled. Spectroquality methanol (MCB) was treated with Na_2EDTA prior to use.

Light Emission Measurements. The apparatus used to measure light emission was previously described.[2d,22] The basic components are a thermostated cell compartment, a Hamamatsu R374 photomultiplier tube, and a Keithley 610A electrometer. Anhydrous sodium sulfate was added to the reaction cell to avoid potential moisture problems and Na_2EDTA was added to avoid possible transition metal ion catalysis. A DBA or DPA solution was allowed to thermally equilibrate in the reaction cell and then the dioxetane solution was added with a λ-pipet. The concentration of the dioxetane solution was determined by a biamperometric iodometric analysis.[23] Light emission as a function of time was obtained from a strip chart recorder. The least-squares method (HP-65 calculator, Stat-Pac 1-22A) was used in the data processing.

Fluorescent quantum yields were measured for DBA and DPA in benzene solution as a function of temperature and relative to quinine sulfate on a Perkin-Elmer MPF-3 fluorescence spectrophotometer. The measured fluorescent quantum yields for DBA and DPA at 45 °C were 0.12 and 0.53, respectively. Activation parameters for DBA fluorescence are $E_a = -5.13 \pm 0.19$ kcal/mol, $\log A = -4.44 \pm 0.14$, and for DPA they are $E_a = -1.23 \pm 0.11$ kcal/mol, $\log A = -1.12 \pm 0.08$ in benzene solution. The relative fluorescence quantum yields for DBA in benzene vs. methanol ($\Phi_f^{DBA}(C_6H_6)/\Phi_f^{DBA}$(MeOH)) were determined in the light emission apparatus at 45 °C, which was fitted with a Bausch and Lomb 250-mm monochromator. Excitation by means of a Pen-Ray mercury penlamp at 365 nm was used. A value of 2.39 was obtained for $\Phi_f^{DBA}{}_{(C_6H_6)}\Phi_f^{DBA}{}_{(MeOH)}$ and this was used to correct the emission data in methanol solvent.

***trans*-Stilbene Isomerization Methods.** Stock solutions of *trans*-stilbene, dioxetane, and 2,6-di-*tert*-butyl-*p*-cresol were mixed and diluted to 1.00 mL. The concentration of the latter radical trap was maintained constant at 0.008 M. The solutions were transferred to 6-mm tubes, with a 4-mm bottom section, which were fitted with a ⅋ joint. The solutions contained in these tubes were degassed on a vacuum line (10^{-4} mm) through three freeze–thaw cycles. The solutions were protected from mercury vapor by two liquid nitrogen traps. The tubes were sealed with a torch under vacuum and then heated in a thermostated bath. GLC analyses for *cis*- and *trans*-stilbene were made on a 7.3% Dow-Corning 550 silicone oil on Varaport-30 support (5 ft × ⅛ in.) at 165 °C with a flow rate of 36 mL/min. The injector and detector temperatures were set at 250 and 240 °C, respectively. Retention times for *cis*- and *trans*-stilbene were 5.3 and 11.0 min, respectively. The concentration of *cis*-stilbene was calculated by using the sum of *cis*- plus *trans*-stilbene as the internal standard. A blank was measured, where the dioxetane was omitted from the solution, to obtain the net amount of *cis*-stilbene that was produced in the thermolysis of the dioxetanes. Solutions containing *trans*-stilbene were protected from light throughout the operation. Plots of $1/\Phi_{App}$ vs. $1/[t\text{-S}]$ were fitted by the least-squares method.

Table II. Correlation of Activation Energies vs. the Efficiency of Triplet Carbonyl from 1,2-Dioxetanes

dioxetane	E_a, kcal/mol	α_{T_1}, %	ref
DMD	23.0	13	2e, this work
PMD	22.9	14	2e, this work
DPD	22.7	1.2	2d, this work
DBD	24.3	22	2d, this work
TPD	23.3	1.9	2b, this work
DAD	20.9	0.41	2a, this work
TMD	26.4 (av)	36	8, 18, 19, this work
TED	30.0	60[a]	15
DMBD	25.2	30[a]	15
DPMD	25	35[b]	14
AD	34.6	15	20
1	23	1.3[c]	17
2	25.6	13[c]	17
3	29.8	21[c]	17
4	24.4	24[a]	8
5	28.6	12[a]	8
6[d]	24.6	36[a]	8
7[e]	23.6	10	9

[a] Normalized to α_{T_1} = 36% for TMD, reported value α_{T_1} = 30%. [b] Normalized to DMD (α_{T_1} = 13). [c] Normalized to α_{T_1} = 36% for TMD, reported value α_{T_1} = 22%. [d] *p*-Dioxenedioxetane. [e] *trans*-3,4-Diphenyl-1,2-dioxetane.

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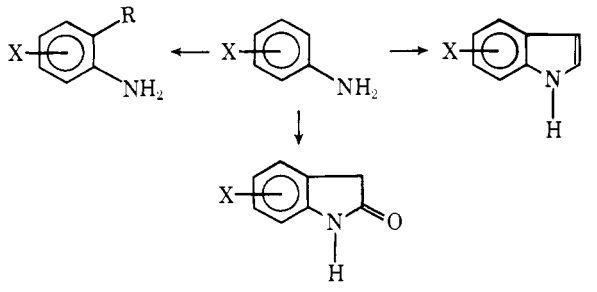
The Ortho Functionalization of Aromatic Amines. Benzylation, Formylation, and Vinylation of Anilines

Paul G. Gassman* and H. Roger Drewes[1]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, and Department of Chemistry, University of Minnesota,[2] Minneapolis, Minnesota 55455. *Received June 2, 1978*

Abstract: New synthetic procedures have been developed for the specific ortho functionalization of aromatic amines. Utilizing reactions which involve the intramolecular rearrangement of ylides derived from azasulfonium salts, processes have been developed which permit the selective introduction of the benzyl, formyl, and vinyl moieties ortho to the amino function of anilines.

Although the use of [2,3]-sigmatropic rearrangements for the selective ortho substitution of aromatic rings was pioneered by Sommelet[3] and extended by Hauser,[4] it was only recently (1972–1977) that extensive synthetic use was made of the rearrangement of ylides derived from *N*-arylazasulfonium salts.[5] These rearrangements provide for a simple, high-yield conversion of anilines into ortho-alkylated anilines, indoles, and oxindoles.[3] Of particular importance is the ability to carry out these conversions over a wide temperature range (down to −78 °C), with mild reagents, and in the presence of a wide range of substituents. Since the crucial step in the reaction sequence involves the [2,3]-sigmatropic rearrangement



of an ylide derived from an *N*-arylazasulfonium salt, little (if any) charge is built up on the aromatic ring. Thus, electron-withdrawing and electron-donating substituents can both be tolerated. In view of the useful interconversions described above, it was of interest to utilize this conceptual approach for the introduction of functionality directly onto the ortho position of anilines. This paper provides the details of our benzylation, formylation, and vinylation of anilines.[6]

Benzylation of Anilines. Synthesis of 2-Aminodiphenylmethane Derivatives

2-Aminodiphenylmethane derivatives are of interest both as intermediates in the pharmaceutical industry and as precursors of fluorenes.[7] Of the various methods reported for the synthesis of 2-aminodiphenylmethane derivatives,[8] the most successful probably involved the dissolving-metal reduction of the corresponding 2-aminobenzophenones. However, a wide range of substituted 2-aminobenzophenones is not readily available, which makes this approach somewhat limited. It appeared that our method for the substitution of anilines might lend itself to the straightforward preparation of these useful intermediates. In order to meet our objectives, we used benzyl phenyl sulfide as our reagent.

Treatment of aniline with 1 equiv of *tert*-butyl hypochlorite followed by excess benzyl phenyl sulfide in methylene chloride at −78 °C gave no azasulfonium salt formation. Since the aryl sulfide apparently was not sufficiently nucleophilic under these reaction conditions, the solvent was changed to one of a higher dielectric constant and the temperature was raised. These

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